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(Continued from page 3 of cover.)

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By Walter C. Schumb and Louis Goldman.

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Equilibrium studies dealing with the system nitrogen-hydrogen-ammonia in electrical discharges are chiefly of early date and the recorded data are not in very good agreement. As distinct from the numerous qualitative observations of early investigators upon the union of nitrogen and hydrogen in electrical discharges, Thénard[1] first noted that when ammonia is formed in the ozonizer from a mixture of nitrogen and hydrogen at one atmosphere the reaction progresses until 3% of ammonia by volume has been formed. Berthelot[2] found that ammonia gas decomposes until the gas mixture contains 3% ammonia, concluding that the reaction is of the reversible type and that equilibrium is thus attained from either side. Le Blanc and Davies,[3] using a stoichiometric mixture of nitrogen and hydrogen at one atmosphere in an ozonizer obtained an equilibrium mixture containing 2.8% ammonia. Günther-Schulze,[4] working in the pressure range 6 to 30 mm., reported that a mixture of nitrogen and hydrogen is not affected by the glow discharge and that ammonia is completely decomposed. In a corona discharge at 20,000 volts and 60 cycles, Wendt and Snyder[5] found 4.1% ammonia in the equilibrium mixture. Recently Westhaver[6] obtained approximately 6% of synthesis in the equilibrium mixture resulting from the action of a glow discharge upon a stoichiometric mixture of nitrogen and hydrogen; and also reported the presence of hydrazine in the products formed from ammonia in the positive column of the discharge. The effect of fresh machining of the surface of the metal electrodes was noted and the temperature of the tube was varied up to 400°. It has been pointed out by de Hemp-

[1] Thénard: Compt. rend., *76*, 983 (1873); Fortschr. d. Phys., *29*, 754 (1873).
[2] Berthelot: Compt. rend., *2*, 1360 (1876); Ann. Chim. Phys., *67*, 218 (1908); Fortschr. d. Phys., *32*, 1020 (1876); Bull. Soc. Chim., *2*, 101 (1876).
[3] Le Blanc and Davies: Z. Elektrochem. *14*, 361 (1908).
[4] Günther-Schulze: Z. Elektrochem., *30*, 386 (1924).
[5] Wendt and Snyder: J. Am. Chem. Soc., *50*, 1288 (1928).
[6] Westhaver: J. Phys. Chem., *37*, 897 (1933).

tinne[7] as well as by others, that the effect of excess nitrogen and of hydrogen on the equilibrium in an electric discharge is not in accord with the requirements of the law of mass action.

The present investigation was undertaken with the purpose of studying the equilibrium in the system nitrogen-hydrogen-ammonia in an electrodeless discharge under known conditions of current strength, frequency, and pressure, over as wide a range as possible. It was proposed, furthermore, to determine the amount of ammonia synthesized—or left undecomposed, as the case may be—not only by observations of the pressure changes resulting from the action of the discharge, but also by direct colorimetric determinations carried out upon the gas mixture when equilibrium had been attained. It was also hoped that new light might be brought to bear upon the known lack of applicability of the law of mass action on the ammonia equilibrium in electrical discharges.

Experimental

Preparation of Ammonia.—Commercial anhydrous ammonia was condensed upon sodium and twice fractionally distilled, the middle portion alone being collected each time. After chilling with liquid air, the bulb containing the solid ammonia was evacuated to .0001 mm. and the ammonia finally collected in the gaseous form in a thoroughly evacuated 3-liter bulb, provided with a mercury seal in place of a stopcock (A in Fig. 1).

Preparation of Nitrogen-Hydrogen Mixture.—A mixture of nitrogen and hydrogen, 1 : 3 by volume, was used in all the experiments upon the synthesis of ammonia. This mixture was obtained by decomposing purified gaseous ammonia at 1.5 mm. in an electrodeless discharge. The oscillator used for this purpose was a single tube set employing a 50 watt UV-203A tube. The operating wave length was 34 m., corresponding to a frequency of 8820 k.c. This set was described in an earlier paper.[8] Experiments had shown that at about 30 m. complete decomposition of the ammonia was effected, as indicated both by the pressure change and by the negative results given by Nessler's reagent with the resulting gaseous mixture. In order to obviate the danger of contamination of the gas mixture by gases driven from the walls by the discharge, the bulb was subjected during evacuation to a discharge operating at a higher current strength than that used subsequently

[7] de Hemptinne: Z. Physik. Chem., *22*, 358 (1897).

[8] Hunt with Schumb: J. Amer. Chem. Soc., *52*, 3152 (1930).

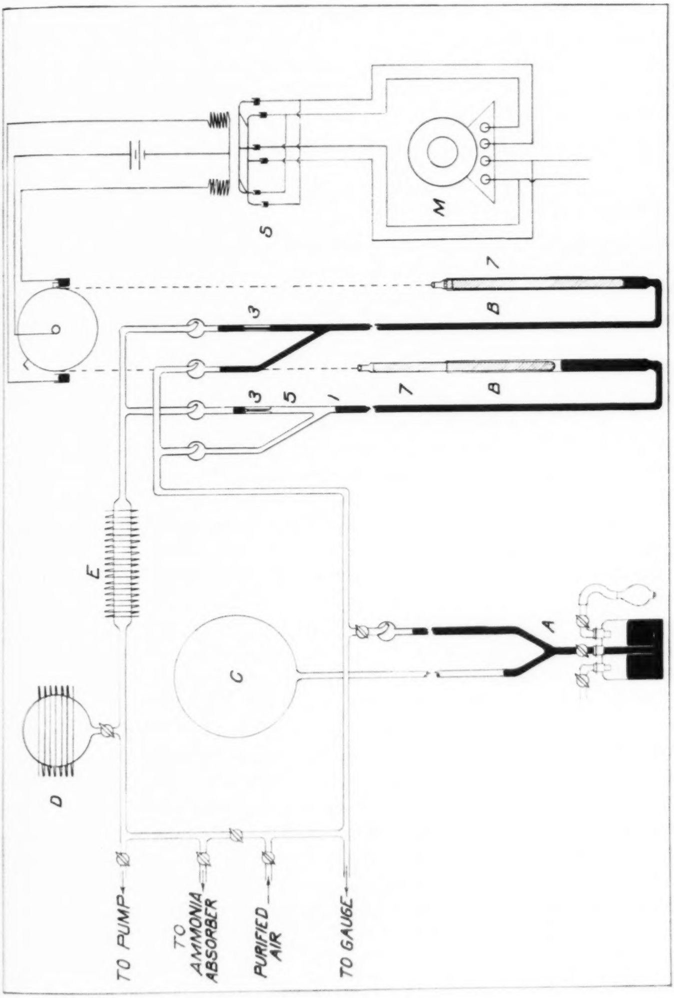

FIGURE 1.

in the decomposition of the ammonia. This process will be referred to below as "preglowing."

Oscillators.—With the spark gap assembly employed in earlier work[9] in which high yields of ammonia had been reported, the wave length obtained was about 260 m. Because of the variability of the characteristics of this assembly, a tube set was designed which could be operated over the range 200–500 m. A standard Hartley circuit was used, with a 250-watt General Electric Company radiotron, type UV-204A (see Fig. 2). With this set a current of 5 to 10 amperes could be obtained in the solenoid between 200 and 300 m. by varying the plate voltage. The solenoid consisted of a nickel-plated copper strip, 9 mm. wide and 1.2 mm. thick, wound as a flat spiral of 24 turns with about 8 mm. spacing between turns, and an inside diameter of 15.5 cm. 14 turns of the spiral were in the oscillating circuit and 24 turns in the grid-to-plate circuit. For operations at lower wave lengths (10–40 mm.) a four tube oscillator operating from the same power pack was available, the detailed wiring of which is also shown in Fig. 2. When the high frequency oscillator was in operation the leads at A, B, C, and D were disconnected from the low frequency oscillator. When the low frequency ocsillator was in operation the leads at A, C, and D were disconnected from the high frequency oscillator.

In the construction of this apparatus a grant from the American Academy of Arts and Sciences was of material assistance, which is hereby gratefully acknowledged. The design and the construction of the oscillators are due to Mr. F. M. Gager, formerly a member of the staff of the Department of Electrical Engineering of this Institute.

Circulation of Gas Mixture.—The mixture of nitrogen and hydrogen was *circulated* through the discharge tube, because it was believed that the yield of ammonia so obtained would be greater than that resulting from the discharge in a static system. It has been demonstrated by van der Wyk[10] and by Briner and Baerfuss[11] that when a stream of nitrogen and hydrogen passes through an electric discharge, the yield of ammonia rises with the rate of flow. These investigators, however, were not studying equilibrium conditions as is the case in the present work. A second advantage of the circulation method in the synthesis of ammonia lies in the fact that the volume of the "dead

[9] Schumb and Hunt: J. Phys. Chem., *34*, 1919 (1930).

[10] van der Wyk: J. Chim. Phys., *25*, 251 (1928).

[11] Briner and Baerfuss: J. Chim. Phys., *17*, 71 (1919).

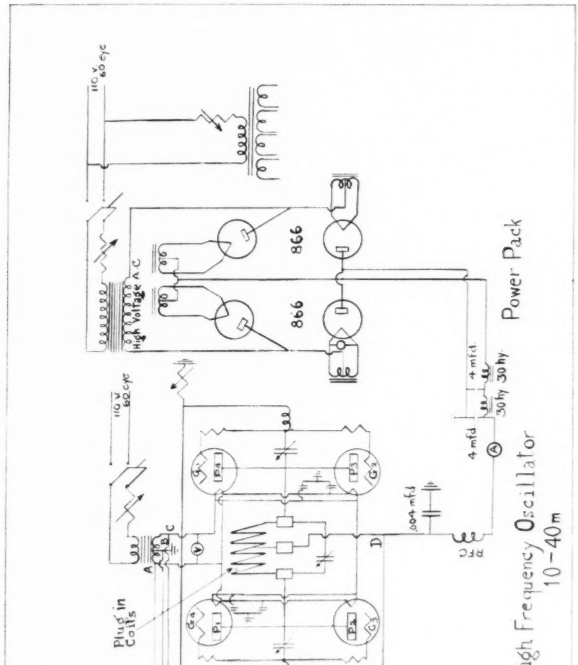
110 V. 60 cyc
High Voltage A.C.
866
866
Power Pack
4 mfd.
30 hy
High Frequency Oscillator
10–40m
Plug in Coils
RFC
P1, P2, P3, P4 are 852
.004 mfd.
Low Frequency Oscillator
200–550 m

FIGURE 2.

space," containing gas that is not subjected to the influence of the discharge, in this method is reduced practically to the volume of the bulb of the McLeod gauge alone, because of which fact the correction which must be applied to the observed change in pressure of the system, in order to be able to calculate percentage of synthesis attained, is reduced to about the magnitude of the experimental error.

The circulation pump is shown in Fig. 1. The two plungers (7) were glass tubes partially filled with mercury which sank by the action of gravity in the two wells, also containing mercury, and were attached by a chain to a sprocket above, which turned upon a shaft geared to a small speed reducer (not shown in the figure) which in turn was operated by a D.C. motor (M). The direction of rotation of the motor was reversed after the proper intervals of time by the rocking switch, or relay (S), which was wired to two contacts on the sprocket. When a plunger sank, the mercury rose in the narrow tube to a point above the capillary (3); when the plunger rose, the mercury fell in the narrow tube to a point below the T, through which gas entered the vacuum left in the upright tube (5). Due to the capillary portion (3), a quantity of mercury remained above (3), sealing the capillary and thus acting as a valve; the time required for the plug of mercury to empty through the capillary was greater than that required for the column of mercury below the capillary to fall to (1) and to rise again to (3). With the rising stroke gas was forced through the mercury valve and so into the rest of the apparatus. The two pistons, operating alternately and in parallel, made about 25 strokes each per minute and brought about a circulation of about 250 cc. of gas mixture per minute at 1 to 2 mm. pressure.

(C) was a 3-liter reservoir in which purified ammonia was stored, confined by a mercury seal. (D) was a liter bulb in which ammonia at 1.5 mm. was completely decomposed by the action of an electrodeless discharge as above described. When the nitrogen-hydrogen mixture had been admitted from (D) into the circulating system at a known pressure, the pumps (B) circulated the gas through the discharge tube (E). This reaction chamber was evacuated and baked at 350° C. for one hour before each run. The pressure in the system before and after the discharge—time being allowed for cooling to the original temperature—was read upon a McLeod gauge.

Study of the Wall Effect.

That the synthesis of ammonia is a wall reaction has been clearly indicated by the work of Pohl,[12] Warburg and Rump,[13] Alsfeld and Wilhelmy,[14] and others. Consequently, to hope for any satisfactory degree of reproducibility in results, the proper conditioning of the walls of the reaction vessel is essential. Preglowing of the reaction tube proved inadequate for this purpose, as erratic values with a general downward trend for the percentage of ammonia synthesized in a series of runs were obtained. It was observed that if the reaction tube was baked while being highly evacuated for one hour at a temperature of 350° C., a reproducible pressure drop could be obtained in a subsequent run. These conditions of temperature and time of baking were adopted as standard procedure in the pre-treatment of the reaction vessel, because it was found that if the tube was baked at 450° C. instead of 350° C., or for two hours instead of one hour, no difference in the pressure drop resulted.

Effect of Increased Surface.—To magnify the effect of the surface exposed in the reaction vessel, a tube was filled with glass wool and thoroughly evacuated. Without further pretreatment a pressure drop was obtained upon a stoichiometric mixture of nitrogen and hydrogen corresponding to a large percentage of synthesis (as high as 36%); successive experiments with fresh gas mixtures and with evacuation between runs, however, showed rapidly diminishing pressure drops, approaching a small value (about 10%). If the tube was now allowed to stand for a number of hours a larger percentage of synthesis was again obtained, but succeeding runs again showed rapidly decreasing values approaching approximately the same final value previously obtained.

The effect of variation in surface is further seen in the results obtained with two tubes of dimensions as nearly alike as possible, in which the nitrogen-hydrogen mixture was subjected to the discharge under the same conditions. Thus a Pyrex tube of 18 mm. inside diameter, 37 cm. long (referred to below as No. 1) containing no glass wool, pretreated by the standard procedure, at 277 m. and 7 amp. gave a reproducible pressure drop of $.062 \pm .002$ mm.; while a similar but different tube (No. 2) under the same conditions gave a pressure drop

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[12] Pohl: Ann. d. Phys., *21*, 879 (1906).

[13] Warburg and Rump: Zeit. f. Phys., *40*, 557 (1927).

[14] Alsfeld and Wilhelmy: Ann. d. Phys., *8*, 89 (1931).

of .045 ± .002 mm. This difference in results shown by the two tubes is discussed below.

In a separate series of experiments, instead of the use of glass wool to afford increased surface, a larger reaction tube, 30 cm. long and 53 mm. inside diameter, was employed. Using this larger reaction tube, the total volume of the *system* was approximately doubled (from about 600 to 1200 cc.), and the surface area of the *reaction tube* alone likewise was about doubled; the pressure drop obtained, however, was nearly the same as that given by tube 2 (.047 mm., at 265 m., 7 amp.). These data indicate that the amount of ammonia formed in the large tube is twice that produced in the small tube. Ammonia formation is, therefore, proportional to the surface area exposed in the reaction tube.

If the reaction tube was baked *after* a run a rise of pressure was noted (the measurement being made as usual after cooling to room temperature). Thus, in a particular experiment, the following data were obtained:

Wave length = 277 m. Current = 7 amp. Reaction tube No. 1

Initial Pressure (mm.)	Final Pressure (mm.)	Pressure after Baking (mm.)	Pressure after a Second Baking (mm.)
1.057	1.000	1.024	1.024

Thus, the ammonia formed by the action of the discharge is in part retained on the walls of the vessel and is later driven out by the baking.

A somewhat perplexing situation was encountered when it was observed that, while subjecting the nitrogen-hydrogen mixture to the electrodeless discharge for 15 minutes gave the same net pressure drop as a 30-minute run, nevertheless a series of 15-minute runs on the same gas mixture (with intervals for cooling and measuring pressure) gave further pressure drops after each run as shown in the following table, which records the pressure drops obtained in successive 15-minute runs on the same gas mixture:

Wave length = 277 m. Current = 7 amp. Reaction Tube No. 1

Initial Pressure (mm.)	Pressure Drops (mm.)					
	1	2	3	4	5	6
1.020	.060	.014	.012	.003	.011	.010
1.026	.063	.010	.010	.008		

Furthermore, if the reaction tube was baked between the successive 15-minute runs, larger pressure drops than those recorded in the preceding table were obtained, as shown in the following table:

Wave length = 260 m. Current = 7 amp. Reaction Tube No. 2
Initial Pressure = 1.012 mm.

Run	Pressure Drop (mm.)	Pressure Rise after Baking (mm.)	Net Pressure Drop (mm.)
1	0.047	0.016	
2	.025	.011	
3	.022	.013	
4	.018	.012	0.060

Discussion.—Consideration of the results of the experiments above described leads us to the following interpretation of the part played by the walls of the reaction vessel in the formation of ammonia. Active particles of nitrogen and of hydrogen, formed in the gas phase, collide upon the wall and form ammonia. The reaction continues until the surface is covered with a layer of adsorbed ammonia, whereupon further synthesis ceases to occur, no matter how long the discharge be continuously operated. At the steady state thus established ammonia evaporates from the wall at the same rate at which it is being formed on the wall. In accordance with the views of J. and W. Taylor[15] on the nature of the dark annular space adjacent to the walls of the discharge vessel, the ammonia adsorbed on the wall would be expected to escape decomposition. These authors point out that the dark space is due to the fact that the negatively charged wall prevents almost completely the entrance of electrons into the gas layer contiguous to

[15] J. and W. Taylor: Proc. Cambridge Phil. Soc., *24*, 263 (1928).

the wall. The adsorbed ammonia therefore, is not subjected to electron bombardment and remains undecomposed.

The observations recorded above, together with other considerations discussed below, may be interpreted in the light of this hypothesis, as follows:

(1) A given tube, used repeatedly with successive portions of a given gas mixture, exhibited a definite fatigue effect—due to the accumulation of adsorbed ammonia on the walls—finally ceasing altogether to bring about synthesis; but by baking the reaction vessel before each run in the manner described, reproducible pressure drops were obtained. The effect of the baking and evacuating is obviously to bring the walls into the same condition before each run by clearing them of adsorbed gas.

(2) A tube filled with glass wool and evacuated gave a much higher yield of ammonia than the same tube without glass wool. Repeated runs with the glass wool, with no pre-baking, gave rapidly diminishing pressure drops approaching a small value, the magnitude of which did not appreciably alter in subsequent runs. The initial high value was caused by the great surface exposed by the glass wool; the rapid decrease in the pressure drops was due to the accumulation of adsorbed ammonia; the constant magnitude of pressure drop obtained after a number of runs was brought about when the surface of the glass wool was covered with adsorbed gas, the evaporation of which during evacuation between runs exposed roughly equal areas.

(3) The difference in the results obtained with two similar tubes under the same conditions, as described above, is not surprising when it is remembered that, although the macrostructure of the two tubes might appear to be very similar, the microstructure of the walls of the tubes may be sufficiently different to account for considerable difference in surface area; and ammonia formation, as previously stated, is proportional to the surface area exposed in the reaction tube.

(4) The pressure rise resulting from baking of the reaction tube after a run is due to the driving out of adsorbed ammonia from the walls.

(5) A series of four 15-minute runs had a much greater effect than a single run of an hour's duration, due to the fact that when the tube is allowed to stand for a short time, opportunity is given for some of the ammonia to evaporate into the gas-filled space, exposing fresh wall surface and hence permitting further synthesis to occur when the discharge is again operated. If the reaction tube is baked in the

interval between runs, the larger pressure drops obtained are due to the fact that baking exposes a greater surface than that resulting from evaporation at room temperature.

(6) *Colorimetric confirmation.*—Furthermore, if the ammonia remaining in the gaseous condition in the tube after a run was thoroughly swept out with well-dried nitrogen, absorbed in very dilute sulphuric acid, and determined colorimetrically (Nesslerization), an additional quantity of ammonia subsequently could be obtained by baking the reaction vessel and again sweeping out the ammonia thus released from the walls of the vessel with dry nitrogen.

The absorption of ammonia was carried out in a glass tube 20 mm. wide and about 70 cm. long, supplied with a series of ten constrictions, the whole tube being held in a position slightly inclined from horizontal. The gas passed slowly over the surface of the absorbing liquid and bubbled through the liquid at the constrictions.

By means of this process a reasonably good check between the amount of synthesis calculated independently from the pressure drops and from the colorimetric determinations was afforded. Unless the reaction tube was baked after operating the discharge, only a fraction of the ammonia formed by the discharge could be swept out by the nitrogen. A typical run which illustrates these facts, furnished the following data:

$I = 7$ amp. $\lambda = 280$ m. Reaction tube No. 2

Initial press. of mixture (mm.)	Pressure drop (mm.)	Press. rise after baking (mm.)	Net press. drop (NH_3 formed) (mm.)	NH_3 in gas phase (before baking) (mm.)	% NH_3 in gas (before baking) (mm.)	NH_3 found colorim. (after baking) (mm.)
1.040	0.042	0.017	0.025	0.008	32	0.023

Similarly, the net pressure drop, 0.060 mm., recorded in the table on page 177 was confirmed colorimetrically, the quantity of ammonia found by Nesslerization corresponding to a pressure drop of .051 mm.

Effect of Variation in Frequency, Current, and Initial Pressure.

In the accompanying graphs, Figs. 3 to 8, the effects of alteration of frequency, current, and initial pressure on pressure drop, over the

range permitted by the apparatus, are shown. In Fig. 3 drop in pressure is plotted against wave length for an initial pressure of 0.55 mm. Fig. 4 shows similarly the results for an initial pressure of 1.05 mm., with currents of 5, 6, 7, and 8 amps. flowing through the solenoid. It will be seen that the pressure drop rises with the frequency at a rate faster than linear. The intensity of the glow was observed to increase with frequency. Figs. 5 and 6 indicate the increase in pressure drop with increasing current, at constant frequency; and fig. 7 shows the

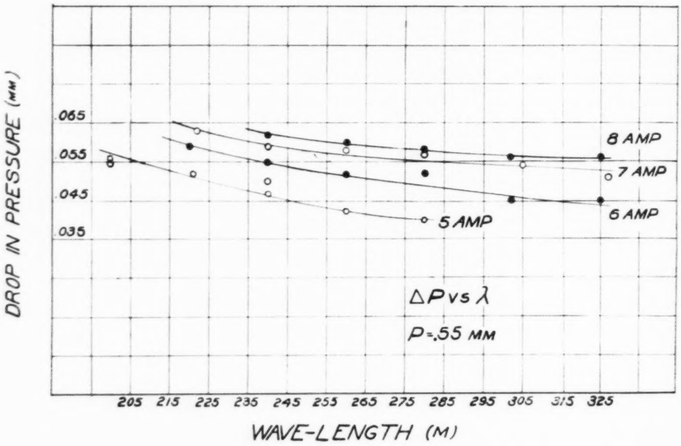

FIGURE 3.

effect of change in the initial pressure upon the drop in pressure obtained. With increasing initial pressures the pressure drop is seen to decrease. In the hypothesis above advanced of the mechanism of the reaction, no indication is given of such an effect of variation in initial pressure; for it would seem that if the reaction proceeded until the walls of the vessel had become inactive due to a film of adhering ammonia molecules, then the drop in pressure should be independent of the initial pressure. Other effects evidently are responsible for the observed results, such as the change in conductivity with changing pressure, and the rise in the mean free path as pressure decreases, which facilitates access of active particles to the walls of the reaction vessel.

It was thought desirable also to observe the effect upon the pressure drop of variation in frequency at *constant energy output* of the solenoid, which, in general, was an unknown quantity. In order to obtain a satisfactory measure of the energy output of the solenoid, the expedient was adopted of observing the rise in temperature brought about when the bulb of a mercurial thermometer was placed approximately at the center of the solenoid (the glass reaction vessel being absent), and the discharge operated at known frequencies and current

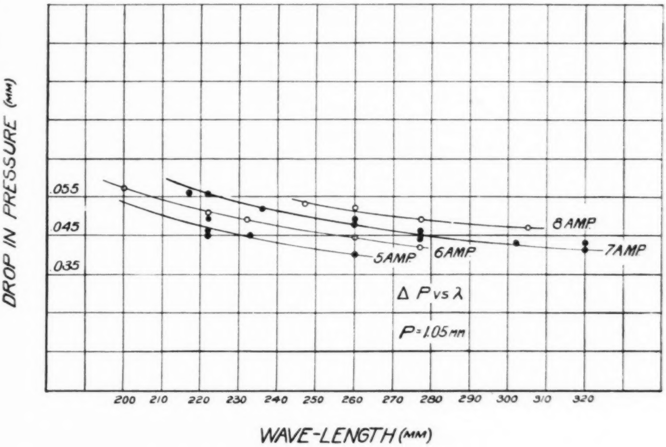

FIGURE 4.

strengths until a constant temperature was reached. When the rise of temperature was plotted against wave length at 5, 6, 7, and 8 amp., a series of parallel lines was obtained. The energy output of the solenoid was then taken as constant for such combinations of wave length and current as gave the same temperature rise. From Fig. 8, wherein pressure drop is plotted against wave-length at constant energy output of the solenoid, it is seen that the pressure drop rises at an *accelerated* rate with increasing frequency; this indicates that frequency has a specific effect upon the pressure drop produced, and that the rise of the latter with frequency is not simply the effect of changing energy output accompanying the change in frequency.

Because of the fact that the pressure drop rises with frequency at

a rate faster than linear, and because the pressure drop obtained at 265 m. and 7 amps. was .047 mm., while at 18 m. a pressure drop of .028 mm. was obtained with the same prebaking procedure, the conclusion may be drawn that at some intermediate frequency the extent of synthesis passes through a maximum. This evidence is not complete, however, as the ampere-turns for the 18 m. measurements were not the same as in the 265 m. measurements, there being no way to determine accurately the current in the solenoid at 18 m. Experimentation is at the present time under way with the object of studying this matter further, by extending the wave length range below 200 m. as far as possible with the Hartley oscillator.

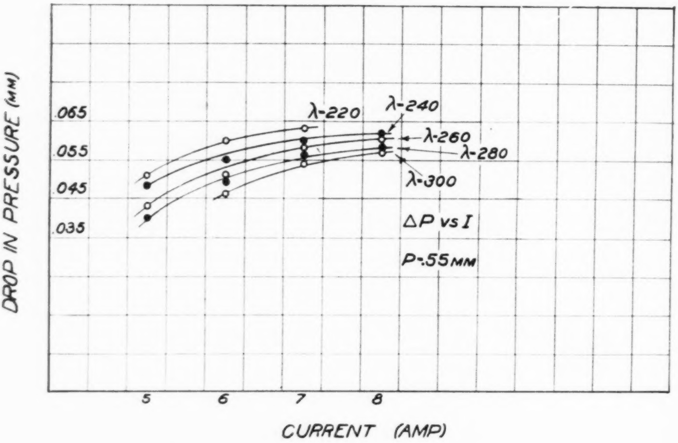

FIGURE 5.

APPROACH TO THE STEADY STATE FROM THE AMMONIA SIDE.

Consideration of the phenomena occurring in the nitrogen-hydrogen mixture in the electrodeless discharge naturally suggests a comparison of the steady state conditions attained in this case with those resulting from the operation of the discharge in ammonia gas. Starting, for example, with ammonia at 0.5 mm., or with the stoichiometric nitrogen-hydrogen mixture at 1.0 mm., it might be expected that under the same conditions and in the same tube the pressure drop obtained with

the second mixture should equal $2P_i - P_f$, where P_i is initial pressure of ammonia and P_f the final pressure of the mixture.

A satisfactory confirmation of this premise was obtained, as will be shown in the following table; but only after due allowance was made for the adsorption of ammonia by the walls of the tube when the gas was admitted after the customary baking and evacuation of the vessel.

The first two columns of the table give the observed initial pressure of ammonia and the values of $(2P_i - P_f)$ after the discharge. The

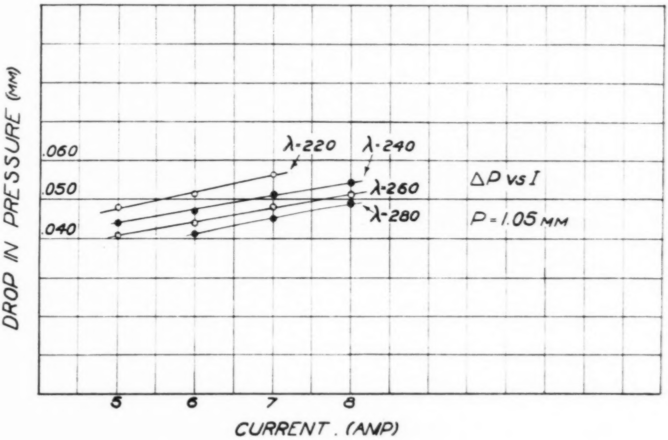

FIGURE 6.

third and fourth columns show the initial pressure and the drop in pressure obtained when the $N_2 : 3H_2$ mixture at about 1 mm. was subjected to the discharge under the same conditions, the tube having been baked and evacuated as usual. It will be noted that ΔP in column 4 is about twice as large as $2P_i - P_f$ in column 2. This lack of agreement, at first sight somewhat puzzling, appears quite reasonable when examined more closely in the light of the hypothesis advanced above. When ammonia is introduced into the freshly baked and evacuated reaction bulb some gas is adsorbed by the walls before the initial pressure is read, and the active area exposed is reduced in extent. When the ammonia gas is decomposed in the discharge only a relatively small surface is left free upon which ammonia may be

formed by recombination of the nitrogen and hydrogen particles so produced.

In order to test this explanation of the lower values of $2P_i - P_f$ (column 2) as compared to ΔP (column 4), a third series of runs was made, as shown in columns 5 and 6, in which the walls of the reaction vessel were "rinsed" with ammonia before admitting the $N_2 : 3H_2$ mixture to be subjected to the discharge. The tube was first well baked and evacuated; ammonia was then introduced at .5 mm. and

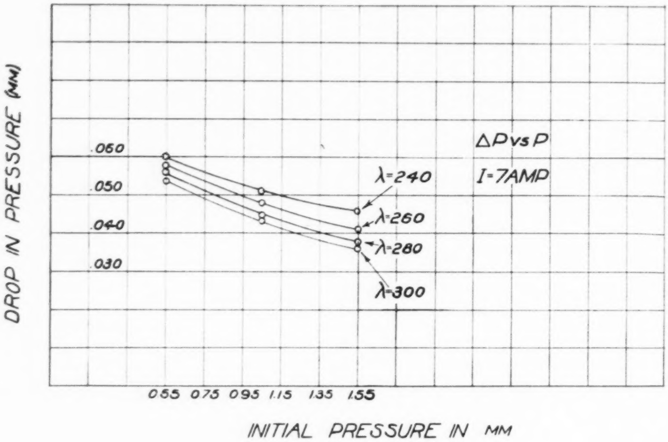

FIGURE 7.

λ = 265 mm. I = 7 amp. Reaction tube, 380 × 18 mm., I.D.

P_{iNH_3} (mm.)	$2P_i - P_f$ (mm.)	$P_{i(N_2+3H_2)}$ (mm.)	ΔP (mm.)	$P_{i(N_2+3H_2)}$ (mm.)	ΔP (mm.)
0.502	0.024	1.056	0.044	1.100	0.022
.480	.020	1.002	.048	1.045	.019
.510	.020	1.016	.045	1.027	.025
.541	.022	—	—	—	—

the tube again evacuated; finally the $N_2 : 3H_2$ mixture was admitted and the run conducted as usual. The agreement observed in a comparison of columns 6 and 2 indicates that the same steady state is

reached whether starting with ammonia at 0.5 mm. or with the nitrogen-hydrogen mixture at 1.0 mm.

Ammonia Synthesis in a Static System.—In conclusion, it is of interest to note, and to interpret in the light of the hypothesis presented above, the effect produced by substitution of a static system for the circulatory arrangement employed in all the preceding work. If, as we have postulated, in the case of the discharge in the nitrogen-hydrogen mixture, synthesis proceeds until the wall becomes covered

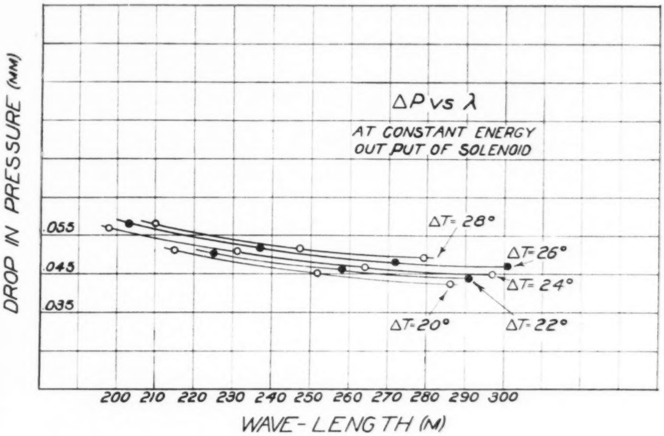

FIGURE 8.

with a layer of adsorbed ammonia, then, given two reaction tubes of equal volumes, one of them a part of a circulatory system such as has been described, the other forming a part of a static system of distinctly less total volume, we should expect to obtain much larger pressure drops with the static system, since the same number of molecules are being removed (as ammonia is formed) from a much smaller volume.

Large pressure drops were in fact observed in a series of experiments with a static system wherein the reaction tube, sealed at one end, was connected directly to the McLeod gauge. At 267 m. and 7 amp., the following data were obtained with the $N_2 : 3H_2$ mixture at about 1 mm.:

Initial Pressure Drop (mm.)	Rise on Baking (mm.)	Net Pressure Drop (mm.)
0.362	0.138	0.244
.364	.141	.223
.382	.152	.230

Although the agreement in the three runs is poorer than that obtained in the runs with the circulatory system, it is, nevertheless, certain that the initial pressure drops are much larger than those noted in the previous work—0.37 mm. in the static method, as compared with 0.046 mm. under the same conditions in the circulatory system. The total volume of the static system was approximately 50 cc. as compared with approximately 550 cc. in the circulatory system.

The distribution of ammonia between the walls and the gas space is about the same in the two cases, but in the circulatory method more ammonia is formed both on the walls and in the gas space, as will be made evident by the consideration of the following data:

	Vol. of System (cc.)	Net press. drop $=NH_3$ formed (mm.)	Press. rise on baking $=NH_3$ released from walls. (mm.)	Total millimols NH_3 formed $\times 10^3$	Millimols NH_3 on walls $\times 10^3$
Circulatory Method	550.	0.028	0.018	0.83	0.53
Static Method	50.	0.23	0.14	0.62	0.38

Summary.

1. A study has been made of the synthesis of ammonia from a stoichiometric mixture of nitrogen and hydrogen, at pressures of from 0.5 to 1.5 mm., when submitted to the influence of an electrodeless discharge operated over the wave-length range 200–330 mm., with current strengths of from 5 to 8 amps. in the solenoid. The calculations of the amount of ammonia synthesized from the observed pressure change, when due provision was made for driving out the gases adsorbed by the walls, were shown to correspond with the quantity of

ammonia contained in the system by colorimetric determinations carried out upon the resulting gas mixture.

2. Since the synthesis of ammonia in this manner is known to be a wall reaction, various expedients were tried to observe the effect of the extent and condition of the wall surface exposed to the reacting mixture, and from the data obtained an hypothesis has been advanced for the mechanism of formation of ammonia in the discharge vessel.

3. The hypothesis proposed accounts for the data obtained in a study of the following aspects of the wall effect:

a. The necessity of adequate pretreatment of the reaction vessel, consisting of evacuation and baking, in order to obtain reproducibility of results.

b. The effect of increased surface by the use of glass wool.

c. The comparison of results obtained under as nearly as possible identical conditions with two different reaction tubes of closely similar dimensions.

d. The comparison of results obtained with a small and with a large tube under like conditions, leading to the conclusion that the formation of ammonia is proportional to the surface exposed.

e. The rise in pressure brought about by baking of the reaction tube after a synthesis run.

f. The continued pressure drops obtained when the same gas mixture was subjected repeatedly to the discharge, with short intervals of time for cooling and measurement of pressure.

g. The approach to the same final state, whether starting with the nitrogen-hydrogen mixture or with ammonia. In the former case "rinsing" of the walls of the tube with ammonia gas, prior to admitting the nitrogen-hydrogen mixture, was found necessary in order that the same final state be realized.

h. The agreement obtained in the estimation of the quantity of ammonia synthesized by pressure measurements and by colorimetric analysis.

4. It has been shown that much larger pressure drops are obtained in a static than in a circulatory system, a fact which is likewise in accordance with the hypothesis referred to above. More ammonia is formed in the circulatory system although the percentage distribution between wall and gas space is the same in both cases.

5. Evidence has been obtained indicating that the percentage of synthesis of ammonia, when plotted as a function of frequency, passes through a maximum.

6. The hypothesis advanced for the mechanism of the synthesis in the discharge leads to the conclusion, which has been repeatedly demonstrated experimentally, that the law of mass action should not be expected to apply to this case, as it is not a homogeneous gas phase reaction.

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